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HIGHWAY RESEARCH REPORT

DEVELOPMENT OF A RAPID SET EPOXY ADHESIVE FOR CALIFORNIA HIGHWAY MARKERS

INTERIM REPORT

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STATE OF CALIFORNIA

BUSINESS & TRANSPORTATION AGENCY

DEPARTMENT OF PUBLIC WORKS

DIVISION OF HIGHWAYS

MATERIALS AND RESEARCH DEPARTMENT

RESEARCH REPORT

NO. M & R 635150

Prepared in Cooperation with the U.S. Department of Transportation, Bureau of Public Roads June 1969

STATE OF CALIFORNIA—TRANSPORTATION AGENCY

RONALD REAGAN, Governor

DEPARTMENT OF PUBLIC WORKS
DIVISION OF HIGHWAYS
MATERIALS AND RESEARCH DEPARTMENT
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Research Report
P. W. O. 635150

June, 1969

Mr. J. A. Legarra
State Highway Engineer

Dear Sir:

Submitted herewith is a research report titled:

DEVELOPMENT OF A RAPID SET

EPOXY ADHESIVE

FOR CALIFORNIA HIGHWAY MARKERS

Herbert A. Rooney
Thomas L. Shelly
Co-principal Investigators

Donald R. Chatto
Co-investigator

Very truly yours,

JOHN L. BEATON
Materials and Research Engineer

REFERENCE: Rooney, Herbert A; Shelly, Thomas L; and Chatto, Donald R; "Development of a Rapid Set Epoxy Adhesive for California Highway Markers", State of California, Department of Public Works, Division of Highways, Materials and Research Department, June, 1969, Research Report No. 635150.

ABSTRACT: Conventional epoxy adhesives reacted with the commonly used polyamine, polyamide or tertiary amine curing agents require 3 to 4 hours to harden in thin films at 75°F, 7 or more hours at 50°F, much longer at temperatures below 50°F and the curing essentially ceases at 30°F.

When used to bond pavement markers to the road surface or make roadway surface repairs with epoxy mortars, such limitations create serious and hazardous obstructions to the flow of traffic.

The California Division of Highways designed and formulated a series of epoxy binders and adhesives based upon the use of a polymercaptan curing agent which cures epoxies in thin films at a rate 7 to 10 times as fast as the conventional nitrogen based materials, and may be used at temperatures of 30°F or lower. This report discusses the development of rapid cure epoxy formulations for the purpose of cementing raised delineating pavement markers to road surfaces.

KEY WORDS: Adhesives, epoxy resins, rapid curing, low temperature, thin films.

ACKNOWLEDGMENT

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The opinions, findings and conclusions expressed in this report are those of the authors and are not necessarily those held by the Bureau of Public Roads.

It is understood that the raw material ingredients mentioned by trade name in this report may be replaced by other materials having the same physical and chemical properties, and that trade names given in this report do not endorse such materials to the exclusion of equal products. No part of the information presented in this report is to be used for promotional purposes.

TABLE OF CONTENTS

INTRODUCTION

The California Division of Highways has designed and experimented with epoxy adhesives for highway use since 1954. In December, 1965, a policy requiring the use of raised pavement markers as a replacement for most painted lines on all future freeways and conventional highways became effective. The epoxy adhesive used, both experimentally and on contract work has been primarily a standard set epoxy adhesive consisting of a modified epoxy resin and a polyamine type hardener. This system, although quite satisfactory in performance, requires 3 to 4 hours cure at 77°F and 7 hours at 50°F to gain enough strength to hold the markers on the pavement under traffic. At temperatures lower than 50°F the cure time of the standard set adhesive increases to such an extent that it is impractical for use on in service roads.

The first rapid setting epoxy adhesives used by this Department were submitted by vendors for trial use in the highway marker evaluation study. In general these adhesives would bond to concrete satisfactorily but did not develop a sufficient bond strength to the markers as did the slower setting standard set epoxy adhesive. Viscosities of these adhesives were sometimes unusually high leading to mixing problems. Some of the earlier adhesives were found to be quite water sensitive as indicated by bond failures to steel and concrete in both tensile and shear loading after water immersion.

The lack of a reliable and constant source of rapid set epoxy adhesive combined with costs from $30 to $40 per gallon led to a research program to develop an economical and satisfactory compositional specification for rapid set epoxy adhesives.

CONCLUSIONS

A rapid set epoxy adhesive, designated as State of California Specification 68-F-44, rapid set type, has been developed and the specification is included in the Appendix.

This adhesive has a pot life of five minutes and a bond strength to concrete of 200 psi in 25 minutes at 77°F. The tensile strength, using steel-to-steel surfaces is 5,000 psi, after 7 days cure at 140°F. The mixing ratio must be 1:1 by volume, ± 5% of either component to achieve the specified properties.

When proportioned and mixed by currently used automatic mechanical devices this adhesive must be maintained at a temperature of 65° to 85°F. The viscosity of the materials at temperatures beyond these limits makes proper proportioning difficult. This adhesive has been used on several large marker installation contracts, and the results have been generally satisfactory. Standard special provisions issued in March, 1969 require that rapid set adhesive be specified only when heavy traffic or cold weather conditions warrant.

The problems encountered so far have been:

1. <u>Viscosity is Sensitive to Temperature</u>

Proportioning difficulties in the field have occurred due to high viscosity when the adhesive was not properly heated in cold weather.

2. <u>Rate of Set is Sensitive to Manufacturing Control</u>

The rate of set of the rapid set adhesive is very sensitive to the proper ratio of curing agent (B component) to epoxy (A component) (see figure 3), because of the following factors which tend to slow the cure rate.

a. Excess air incorporation in the B component.

b. Variable density of the aromatic oil extender.

This difficulty has resulted in the adhesive sometimes requiring up to 35 minutes to achieve 200 psi bond strength. Inspection of Figure 3, however, shows that the final strength under dry conditions of the adhesive is not overly sensitive to the ratio of curing agent to epoxy. The further research will be directed towards correcting this difficulty with the rate of set.

Cost:

The cost of this adhesive has been about $12.00 per gallon as compared to about $6.00 per gallon for the standard set adhesive in 1,000 gallon orders.

A. PRELIMINARY INVESTIGATIONS

1. Medium Set Epoxy Adhesive

The initial steps in the search for a faster setting epoxy adhesive involved the development of a "medium set" adhesive. However, a formal specification was never issued due to a need for an even faster setting product. The medium set formulation was intended to have a pot life of 10 minutes minimum, thus permitting hand mixing of the two components. A bond to concrete of at least 200 psi in 40 minutes at 77°F and 200 psi minimum at 50°F in 80 minutes was desired. Other physical requirements selected such as shear strength and viscosity at 77°F were the same as the standard set epoxy adhesive.

One of the most critical requirements for a fast setting epoxy adhesive is its ability to cure rapidly in thin films, as occurs in the adhesive bond between the marker and the road surface. An epoxy system cannot be labeled as "fast setting" or "medium setting" on pot life alone; for example, the standard set adhesive has a pot life of 8 minutes but thin films require three to four hours at 77°F to produce the required 200 psi bond strength.

In order to obtain fast thin film strength a high functional polymercaptan resin (Dion 3-800), made by Diamond Shamrock Company, was used as the basis for the "B" or hardener component. The more conventional types of amine and polyamide hardeners do not provide the desired speed of curing in thin films. The boron trifluoride type curing agents when used alone produce rapid cure of the epoxy, but acidic residues in the cured epoxy destroy the bond to concrete.

The Dion polymercaptan can be used alone with an epoxy resin but exceedingly slow cure times result. In order to achieve fast thin film cures, a co-curing agent must be used with the Dion. Preliminary investigation involved the screening of a number of primary and tertiary amines for possible use as co-curing agents.

Method of Screening

The Stoichiometric level of Dion polymercaptan, as supplied by Diamond Shamrock, is 150 parts by weight when used with 100 parts of an epoxy resin having a weight per epoxide equivalent (WPE) of 180-200. When an amine co-curing agent is used, depending on the reactivity of the amine, a correspondingly smaller proportion of Dion polymercaptan must be used. For example, if 100 parts of Dion polymercaptan are used, representing $100/150 \times 100$ or 66.6% of total curing agent, a co-curing agent must make up the remainder of 33.4%. Thus, if an amine requires 10 parts per 100 parts of epoxy resin for stoichiometric cure, then the amount required with 100 parts of Dion is 33% of 10 or 3.3 parts. Using this relationship in compounding initial mixes, thin films were cast and rate of hardening observed and timed. As a measure of hardening rate, the Shore D durometer was used. It was found by experiment that a minimum Shore D of 35 was necessary if the adhesive was to develop a bond strength of 200 psi to concrete.

The following amines were used as co-curing agents at various levels of Dion polymercaptan and amine. The epoxy resin used was Ciba 6004 with 3 phr (parts per hundred of resin) of butyl glycidyl ether as a reactive diluent.

1. Dimethylaminoethanol - Pennsalt #272 Hardener
2. Diethylene triamine - DETA
3. 2,4,6-Tri(dimethylaminomethyl) phenol - DMP 30
4. Tetramethyl ethylenediamine - TMEDA
5. Octadecyldimethylamine - Armeen DM18D
6. Hexadecyldimethylamine - Armeen DM16D
7. Benzyldimethylamine - Aldrich Chemical
8. N-N dimethylcyclohexylamine - Abbott Labs.
9. Triethylene-diamine 33% solution - Dabco 33LV.

The most promising co-curing agent was DMP 30, which gave hard, nontacky films. Subsequent work was then concentrated on the DMP 30-Dion polymercaptan system.

Selection of Epoxy Resin

With Ciba 6004 and 3 phr butyl glycidyl ether, various levels of Dion polymercaptan from 70 to 150 phr were tried, using DMP 30 as co-curing agent. Dion polymercaptan levels of 100, 125 and 150 gave increasingly soft thin films which failed tensile bond and shear tests to concrete. The 70 and 80 phr levels passed the tensile bond to concrete but failed the concrete shear test. Modified Shell 815 epoxy was tried (11% butyl glycidyl ether) but failed to meet tensile bond and concrete shear tests. The unmodified Shell 828 epoxy resin was tried and produced excellent tensile bond to concrete with 70 phr of Dion polymercaptan. Subsequent work was then centered around the system Shell 828, DMP 30 and Dion polymercaptan.

Shelf Stability

At this stage of the investigation it was found that pot lives of various mixes were increasing with storage time. For example, a particular mix would have an original pot life of 3-1/2 minutes, but after 5 days the same components would give a pot life of 7 minutes and after a shelf life of 10 days, gave a pot life of 11 minutes. Upon investigation it was learned that the Dion polymercaptan 3-800 contained reactive side chains that slowly combined with the DMP 30 on storage thus lowering the catalytic effect on the polymer formation when mixed with the epoxy component. This condition was remedied with Diamond Alkali's Dion 3-800 LC having no side chains. The 3-800 LC proved to have a stable shelf life with DMP 30 and has been used in all subsequent work.

Level of Dion Polymercaptan

Epoxy systems can be designed with Dion polymercaptan levels from 30 to 150 phr using DMP 30 as co-curing agent. In general, the lower the Dion level (with 100 parts of epoxy resin) the harder and more brittle the film produced. High levels (80 to 150 phr) gave softer and more pliable films. For bonding to concrete a level from 50 to 70 phr gave the best results. A 60 phr level was adopted because the 70 phr level gave poorer shear values after soaking in water for 1 week and the 50 phr level required more solid fillers to balance the 1 to 1 by volume mixing ratio between component A and B with resultant higher viscosity.

DMP 30 Level

Experimentally, using unfilled mixes and measuring the thin film cure times and Shore D hardness, 10 parts of DMP 30 gave the fastest cure time when used with 60 parts of Dion and 100 parts of Shell 828 resin. This level of DMP 30 is 4 parts over the stoichiometric requirement but did not show any adverse effects in bond and shear strengths to concrete.

Control of Pot Life

A 60 phr level of Dion with 10 parts DMP 30 with 100 grams Shell 828 gave a pot life of 3 minutes in 170 gram mass. For the medium set adhesive a pot life of 10 minutes was required. The required pot life may be obtained by cutting back in the amount of co-curing agent but this slows down thin film hardening time so that the required 200 psi can no longer be met in 40 minutes. Boron trifluoride phenol polyethylene glycol complex used in the proportion of 4 parts per 10 parts of DMP 30 increased the pot life to 10 minutes, still retaining the concrete bonding requirements, but this material is very hygroscopic and costly ($7.50/lb.).

The tri-2 ethylhexanoate salt of DMP 30 was tried as a catalytic curing agent. This is made by reacting 1 mole DMP 30 with 3 moles of 2-ethylhexanoic acid and varying amounts used as a catalyst. This curing agent causes an excessive decrease in the reaction rate of the Dion - 828 system. When the ratio of hexanoic acid is adjusted to give a partial neutralization of the DMP 30, a controlled gel time can be realized by adjustment of this ratio. 10 parts of DMP 30, 60 parts Dion polymercaptan and 1.4 parts of 2-ethylhexanoic acid gives a pot life of 10 minutes, still retaining the necessary bonding requirements and rate of cure in thin films.

Pigmentation and Viscosity

Pigmentation is required in both components to aid in mixing and to provide the proper degree of thixotropy. The A component is white and the B component black. When properly mixed a uniform gray color results with no streaks of either white or black. Titanium Dioxide is used for white pigmentation in the A component and carbon black in the B component.

Viscosities of the unmodified 828 epoxy resin and the Dion mercaptan are both very high at 77°F and change rapidly with changes in temperature as shown in Figure 1. The viscosity - temperature curve for the modified Shell 815 epoxy is also shown. The correct pigment and filler loading of components A and B are critical if proper mixing with a workable viscosity is to be achieved when the components are mixed prior to use, especially at temperatures near 55°F, which are common in California coastal areas during summer months. Conversely the epoxy should not become too fluid when used at temperatures of 100 + °F which are common in the interior valleys during summer months. To aid in controlling the flow properties of each component the addition of a thixotrope is necessary. The thixotrope not only provides easier mixing but also prevents excessive adhesive flow from under the pavement marker when placed on the roadway. The ratio of the viscosities at 0.5 rpm to 2.5 rpm using a Brookfield Viscometer, is a measure of the degree of thixotropy of the filled components. This ratio represents the slope of the curve of viscosity with respect to rate of shear (rpm) and is typical of non-Newtonian flow as shown in Figure 1.

Colloidal silica, which had been used as a thixotrope in the standard set epoxy adhesive, was tried and produced excellent flow properties when initially made but in storage at room temperatures, over 50% of the original viscosity was lost in the epoxy A component. Accelerated oven aging at 115°F of various colloidal silicas, including suggested improved methods for incorporating the silica into the mix, all showed complete lack of stability. An organic thixotrope, Thixotrol ST which is a hydrogenated castor oil made by Baker Castor Oil, was submitted for testing. The Thixotrol was found to have excellent oven aged stability and thixotropic properties and was adopted as part of the medium set formula. The Thixotrol ST requires at least 160°F with high shear for dispersion on the Cowles dissolver. This led to large amounts of air being entrapped during dispersion in the filled components A and B. This condition upsets the 1:1 volume mixing ratio since the proper ratio of epoxy and hardener would not be reacted. In our laboratory, satisfactory de-aeration was obtained by heating to 175°F and evacuating to 30 inches Hg. A maximum air content of 2.5% by volume is considered satisfactory.

Modifiers, Diluents and Fillers

Since both the epoxy resin and the Dion polymercaptan hardener have relatively high viscosities, efforts were made to reduce the viscosity to permit higher solid filler loading to decrease chemical costs and permit more favorable flow properties for easier mixing. For the A component the following reactive diluents were tried:

1. Shell 871, a diglycidyl ester of linoleic dimer acid.
2. Epi-Rez 5044, an aliphatic diglycidyl ether.
3. Ciba RD1, butyl glycidyl ether.
4. Ciba 1359, resorcinol diglycidyl ether.
5. Epi-Rez 5023, aliphatic diglycidyl ether.
6. 3M Cardolite.
7. Ciba RD2, 1,4-butanediol diglycidyl ether.
8. Ciba Epoxide No. 7, a mixture of aliphatic C_8-C_{10} glycidyl ethers.

All provided viscosity reduction but only one, Ciba 1359, did not slow down the thin film cure rate. The Ciba 1359 has conflicting evidence of being carcinogenic and its use was not considered further.

In the B component the following diluents were tested:

1. Nonyl phenol
2. Di-nonyl phenol
3. Piperidine
4. Di-butyl phthalate

5. Mobilsol 66

6. Mobilsol 44

7. Pine Oil

8. Furfuryl alcohol

9. Thiokol LP3

The only materials of practical use were Mobilsol 66 and the Thiokol LP3. The others usually slowed down the thin film cure rate even though in some instances the mass pot life was accelerated, as was the case with nonyl and di-nonyl phenol and furfuryl alcohol. As will be shown subsequently in this report, the thin film cure of the system may be accelerated using nonyl phenol as a diluent in component B if an excess of DMP 30 is used.

The Mobilsol 66 was chosen as the most suitable non-reactive diluent for the B component due to its compatibility, low viscosity and lower price per pound ($0.22) as compared to the Thiokol polysulfide ($1.00). Up to 15 parts Mobilsol 66 by weight may be used with 60 parts Dion and meet the required curing time; in amounts over 15 parts the system becomes too dilute and thin film reaction time is slowed.

Conventional talc filler for the B component gave high viscosities of the filled systems. For example, using Sierra N-S Silver Talc (70 micron particle size maximum) Brookfield Viscosity of 250,000 centi-poise was obtained. This was considered too high, especially for hand mixing at temperatures around 55°F. The use of Ballotini glass spheres (average size about 40 microns) in the same system gave viscosities around 150,000 centi-poise, which is considered suitable for hand mixing. The spheres have no thixotropic properties and may be loaded in quantities greater than conventional talcs and other inorganic fillers to a higher degree without excessive viscosity increases.

Wetting Agents

Bālab bubble breakers, Tween 20 and Dow Corning Anti-foam Q were tried as aids in wetting and assisting in the de-aeration of the filled components. The Anti-foam Q was found to be the most effective both in pigment wetting and in the ease of releasing the entrained air under vacuum.

Medium Set Formula

Component A - White

	Lbs.	Gallons	Lbs/100 Gallons	% By Weight
Shell Epon 828	100.00	10.31	909.09	87.90
Thixotrol ST	1.50	0.18	13.64	1.32
TiO_2	2.00	0.06	18.18	1.76
Talc N.S. Silver	10.16	0.44	92.36	8.93
Anti-foam Q	0.10	0.01	0.91	0.09
	113.76	11.00	1034.18	100.00

Component B - Black

	Lbs.	Gallons	Lbs/100 Gallons	% By Weight
Dion 3-800 LC	60.00	6.22	545.45	50.29
DMP 30	10.00	1.23	90.91	8.38
2-Ethyl Hexanoic Acid	1.40	0.19	12.73	1.17
Mobilsol 66	15.00	1.65	136.36	12.57
Carbon Black	0.10	0.01	0.91	0.09
Thixotrol ST	1.50	0.18	13.64	1.26
#3000 Ballotini Spheres	31.20	1.51	283.64	26.15
Anti-Foam Q	0.10	0.01	0.91	0.09
	119.30	11.00	1084.55	100.00

Component Properties

Viscosity - Measured with Brookfield Viscometer Model RVT with Model C. Helipath stand and TE spindle. Viscosities in centipoises:

Component A

Temperature	5 rpm	2.5 rpm	0.5 rpm	0.5 rpm/2.5 rpm
77°F	100,000	130,000	300,000	2.3
55°F	480,000	620,000	1,100,000	1.8

Component B

Temperature	5 rpm	2.5 rpm	0.5 rpm	0.5 rpm/2.5 rpm
77°F	175,000	220,000	500,000	2.3
55°F	470,000	640,000	1,100,000	1.7

The ratio of viscosities at 0.5 rpm/2.5 rpm is a measure of the thixotropy of the filled components. This ratio represents the slope of the curve of viscosity with respect to rate of shear and is typical of non-Newtonian flow. A value of 2.0 or better is considered suitable to prevent adhesive flow when the marker is applied to a roadway having a steep grade or superelevation. Curves for both of the components are shown in Figure 1.

Density of Components Lbs/Gal. at 77°F.

	Calculated	Measured	% Error
Component A	10.34	10.17	1.6 low
Component B	10.84	10.67	1.6 low

When components are mixed on a volume basis, densities of each component should be close to theoretical to keep the epoxy and hardener components in proper balance. An error of ± 2-1/2% is considered tolerable.

The organic thixotrope Thixotrol ST requires high shearing at a temperature of 160°F. With the high viscosity materials Shell Epon 828 and Dion polymercaptan 3-800 LC this procedure has produced excess air entrainment with the Components A and B resulting in densities up to 16% low. In this work it has been found necessary to shear the pigments in a Cowles dissolver at 5,000 rpm to a temperature of 160°F. The material is then evacuated at 25 to 29 inches of Hg at a temperature of 175°F. About 1/2 hour is necessary to satisfactorily de-aerate a pint mass.

Physical Properties of Mixed Components

Medium Set

Gel Time (170 gram mass) = 10 minutes at 83°F ambient
12 minutes at 75°F ambient

Tensile Bond to Concrete at 77°F (2" Diam. Steel Cap)

30 minutes - 640 lbs - 204 psi - cohesive break in epoxy.
35 minutes - 725 lbs - 231 psi - cohesive break in epoxy.
40 minutes - 950 lbs - 301 psi - cohesive break in epoxy.

The time reported refers to the actual time of contact between a steel cap and the concrete surface, with the adhesive as the bond.

Tensile Bond to Concrete at 50°F.

60 minutes - 1000 lbs - 318 psi - cohesive break in epoxy.
65 minutes - 1400 lbs - 445 psi - cohesive break in epoxy.
70 minutes - 1600 lbs - 509 psi - cohesive break in epoxy.

Double Lap Shear Strength

24 hour cure at 77°F - 1804 psi - concrete break.
24 hour cure at 77°F + 1 week fog room - 1045 psi - adhesive break.
24 hour cure at 77°F + 1 week water submersion - 1041 psi - adhesive break.

Tensile bond to concrete, cured 24 hours at 77°F - 733 psi - concrete break.
24 hour cure + 1 week water submersion - 605 psi - concrete break.

Bond to the roughened bottom of a reflex reflector marker (as now manufactured) averaged 356 psi with the break in the epoxy adhesive after a 24 hour cure at 77°F.

Bond to ceramic nonreflective markers "as received", averaged 489 psi showing an adhesive break between the markers and the adhesive after a 24 hour cure at 77°F.

This formula for a medium set epoxy adhesive represents the first compositional adhesive developed using polymercaptan curing agents and meets all of the bonding requirements to concrete, but the adhesion to highway markers was very much below that obtained with the standard set adhesive. With the standard set epoxy, adhesive bond strengths over 1,000 psi were obtained to ceramic markers and about 700 psi to the reflex reflector markers. The reflex reflector markers originally manufactured contained a resin rich bottom surface to which it was difficult to bond. Sanding the resin rich bottom surface in some cases increased the bond strength about four fold. The reflex reflector markers currently produced have a roughened bottom which bonds satisfactorily to the epoxy adhesives.

2. <u>Fast Set Epoxy Adhesives</u>

After the development of the medium set epoxy adhesive a "fast set" epoxy adhesive was developed which would have a pot life of about 2 minutes and would be suitable for machine mixing only. This fast set epoxy adhesive would reach a tensile strength of 200 psi to concrete in 12 minutes at 77°F. It was later decided that this pot life was too short when our present "rapid set" formulation was developed with a pot life of about 5 minutes.

To convert the medium set formula to the fast set type necessitated an increase in the co-curing agent DMP 30 and removal of the 2-ethyl hexanoic acid to increase the reaction rate.

<u>Composition</u>:

Component A White - Same as Medium Set Component A

Component B Black

	Lbs.	Gallons	Lbs/100 Gals	% By Weight
Dion 3-800 LC	60.00	6.22	545.45	44.57
DMP 30	13.00	1.60	118.18	9.66
Carbon Black	0.10	0.01	0.91	0.07
Thixotrol ST	1.00	0.12	9.09	0.74
Anti-foam Q	0.10	0.01	0.91	0.07
#3000 Ballotini Spheres	57.64	2.79	524.00	42.85
Mobilsol 66	2.77	0.25	25.18	2.06

Component A and B are mixed 1:1 by volume.

Properties of Mixed Components:

Pot Life (170 grams) - 2-1/2 minutes at 77°F.

Bond to Concrete at 77°F.

12 minutes - 267 psi - cohesive break in epoxy.

Bond to Concrete at 50°F.

18 minutes - 255 psi - cohesive break in epoxy.
22 minutes - 478 psi - concrete break in epoxy.

Double Lap Shear Strength

24 hours cure at 77°F - 1453 psi - concrete break.
24 hours + 1 week fog room - 788 psi - concrete break.

Bond to the roughened bottom of reflex reflector markers and the ceramic nonreflective markers was 180 and 265 psi respectively, failure occurring in the adhesive. The fast set formula had less adhesion to highway markers than the medium set formula but was satisfactory in speed of cure and adhesion to concrete.

B. RAPID SET EPOXY ADHESIVE

FOR AUTOMATIC MIXING AND EXTRUSION EQUIPMENT

Due to the increased activity in marker installations on existing freeways and urban roadways, contractors have been using machine mixed epoxy adhesive almost exclusively. It was decided to abandon the use of "medium" and "fast" set epoxy adhesives and to formulate a "rapid" set type which could be readily applied by machine mixing procedures and provide a strong bond to concrete and pavement markers. A pot life of about five minutes was chosen in order to allow the applicator more time to place and align the markers than could be permitted with the fast set adhesive.

As indicated previously in this report, the medium and fast set adhesives developed were relatively poor in adhesive strength to highway markers (ceramic, reflective and polyester types). A re-evaluation of the Dion-polymercaptan-DMP 30 system was necessary to achieve improved marker adhesion. Concurrently the water absorption characteristics of several epoxy systems were investigated to try to improve the water resistance of the Dion-polymercaptan system.

(1) Bond to Markers

A medium set system using Thiokol LP3 as a diluent in component B was checked for adhesion to highway markers. It was found that the bond strength was double that of the previously described medium set formula. This led to further investigation of the Thiokol LP3 system. Experimental formulas are listed in Table 1 of the Appendix, with the bond strength to various highway markers. Formulas 1 and 2 in Table 1 represent typical values obtained using a 2-inch diameter sandblasted steel cap bonded to the bottom surface of the markers and cured for 24 hours at 77°F. Bond strength was determined by tensile load applied to the steel cap at a rate of 5,000 lbs/min. in a Baldwin Testing Machine. The most significant development in these tests was the fact that formulas 3 and 4 with 2 hour cure had 3 to 4 times the strength of the 24 hour cured specimen. This was interpreted as embrittlement which became noticeable only in the more fully cured specimens. Increasing the Dion polymercaptan levels from 60 to 70 parts as in formulas 5 and 6 gave a more flexible system with good bond strengths after 24 hours cure at 77°F. Bond strengths approached the tensile strength of the ceramic and the filler used in the sanded reflex reflector markers, as the markers themselves failed before the bond strength was exceeded. In formula 6, Mobilsol 66 was substituted for the Thiokol LP3 and equivalent results were observed. From this work a preliminary rapid set formula was determined, with a base of 70 parts Dion polymercaptan using Thiokol LP3 as a diluent.

(2) Preliminary Rapid Set Formula Am 50

Component A - White

	Lbs.	Gallons	Lbs/100 Gals	% Weight
Shell 828	100.00	10.31	952.39	95.58
RG144 Asbestos	3.00	0.14	28.57	2.87
TiO_2	1.62	0.05	15.43	1.55
		10.50	996.39	100.00

Component B - Black

	Lbs.	Gallons	Lbs/100 Gals	% Weight
Dion 3-800 LC	70.00	7.25	666.67	62.16
DMP 30	7.00	0.86	66.67	6.22
LP3	15.66	1.48	149.14	13.91
Carbon Black	0.10	0.01	0.95	0.08
Talc N. S. Silver	17.55	0.76	167.14	15.58
RG144 Asbestos	2.00	0.10	19.05	1.78
2 Ethyl hexanoic Acid	0.30	0.04	2.86	0.27

In the above components RG144 asbestos (Union Carbide) has been substituted for colloidal silica because of the viscosity instability exhibited by the latter in prolonged storage of the A and B components. Thixotrol ST is also an excellent thixotropic agent but requires high shear and temperatures. Asbestos was selected as a thixotropic agent for economic reasons, its cost being 10 cents per pound against a Thixotrol ST cost of 70 cents per pound. Asbestos has shown some vehicle separation on oven aging at 115°F but is readily re-dispersed to yield the original viscosity and thixotropy.

Viscosity at 77°F TE Helipath Spindle, Centi-poises, Formula Am 50

	5 rpm	2.5 rpm	0.5 rpm	Shear Ratio (R)*
Component A	130,000	230,000	525,000	2.3
Component B	120,000	160,000	325,000	2.0

Viscosity at 55°F TE Helipath Spindle, Centi-poises

	5 rpm	2.5 rpm	0.5 rpm	Shear Ratio (R)*
Component A	600,000	760,000	1,200,000	1.6
Component B	450,000	520,000	750,000	1.4

$$* \ R = \frac{\text{Viscosity at 0.5 rpm}}{\text{Viscosity at 2.5 rpm}}$$

Properties of Mixed Components 1:1 by Volume A to B

Pot Life - 6-1/2 minutes

Bond to Concrete at 77°F

25 minutes - 293 psi

Bond to Concrete at 50°F

40 minutes - 318 psi

Tensile Bond to Concrete

24 hours cure at 77°F - 574 psi concrete break.
24 hours + 1 week water immersion - 281 psi - adhesive break.

Shear Strength to Concrete

24 hour cure at 77°F - 759 psi - adhesive break
24 hours + 1 week water immersion - 582 psi - adhesive break.

Bond to High Strength Ceramic Markers

24 hour cure at 77°F - 2125 psi - marker failure.
With post cure 48 hours at 140°F + 24 hours at 15°F - 2129 psi - marker failure.

Bond to Sanded Reflex Reflector Markers

24 hour cure at 77°F - 800 psi - marker failure
7 day water absorption (per ASTM D570-59T) - 3.70%

Adhesion to markers had been improved, especially with the ceramic type, the adhesion being more than double the adhesive strength compared to the first medium set formula.

Although the bonding to markers has been improved, shear strength is low (due to higher Dion polymercaptan level) and water absorption high, which is reflected in low wet shear and tensile strengths against concrete.

The next phase in development was to investigate the water absorption of various systems.

(3) Water Absorption

To determine the differences in water absorptions of various levels of Dion polymercaptan, unfilled mixes were cast between Mylar sheets using 1/8-inch spacers between glass plates to obtain a flat smooth surface. After curing 24 hours at 77°F specimens 1" x 3" x .125" were die cut from the cast sheets. Edges were sanded smooth. Using stoichiometric ratios of Dion polymercaptan and DMP 30, mixes were made using from 10 phr Dion to 70 phr Dion with 100 grams Shell 828 resin. Proportions are shown in Table II with 6 day water absorption results. Also shown is the rate of thin film cure as approximated by the Shore D hardness with time in minutes of cure.

Observation of the data in Table II indicates the higher the Dion polymercaptan level, the more water absorption. Lower levels of Dion polymercaptan yield more water resistant systems, except in case of the 10 phr, but examination of the thin film cure times show a decrease in the rate of cure as the Dion polymercaptan level is lowered. A Shore D hardness of 35 to 40 is required in order to meet the 200 psi bonding requirement to concrete. All levels below 70 parts also showed increasing brittleness when fully cured.

(4) Dion Polymercaptan-Aminoethylpiperazine-DMP 30 System

The standard set epoxy adhesive, a polyamine cure type, has a low water absorption value of 1% in 7 days. The curing agent for this system is N-aminoethyl piperazine with nonyl phenol (NOP) as flexibilizer and diluent. If the Dion polymercaptan system could use AEP or NOP then water resistance might be improved. A series of tests was run using different levels of AEP and NOP as shown in Table III. DMP 30 was used in some cases to speed thin film cure. Stoichiometric requirements were calculated as follows: If 30 parts Dion polymercaptan is used, this represents $\frac{30}{150} \times$ 100 or 20% of the stoichiometric amount of Dion when no co-curing agent or other curing agent used. The remaining 80% is other curing agents or co-curing agents. If AEP is used then the amount required is .80 x 23.2 or 18.6 parts, since the theoretical amount of AEP required to cure 100 grams epoxy resin is 23.2 parts. If both AEP and DMP 30 are used then amounts are proportioned the same, using 10 parts DMP 30 as theoretical amount to cure 100 grams of epoxy resin.

Examination of Table III shows the AEP system to be too slow in thin film for a rapid set adhesive. Of particular interest is the effect of excess DMP 30 in increasing the water absorption, especially at Dion polymercaptan levels of 50 and 60 parts. Nonyl phenol effectively reduces the water absorption at 10 and 20 parts; at 30 parts of NOP no great advantage is gained. The AEP level does not appear to have as much effect in water absorption as does excess DMP 30. Although this system is too slow for a rapid set type adhesive, good bonding strengths were obtained in a formula having the following composition:

Component A	Pounds
Shell 828	100.00
RG144 Asbestos	3.0
TiO_2	1.62
Component B	
Dion 3-800 LC	40.00
AEP	17.00
NOP	20.00
DMP 30	1.00

Component B (Continued)	Pounds
Carbon Black	0.10
RG144 Asbestos	2.00
Talc N.S. Silver	34.87

Physical Tests

Pot Life - 5 minutes

Bond to Concrete at 77°F.

35 minutes - 64 psi - cohesive break in epoxy.
60 minutes - 220 psi - cohesive break in epoxy.

Bond to Ceramic Markers

24 hour cure at 77°F - 2073 psi - broke markers.

Bond to Sanded Reflex Reflector Markers

24 hour cure at 77°F - 1000 psi - broke marker

Tensile Bond to Concrete

24 hour cure at 77°F - 674 psi - concrete break.
24 hours + 1 week water immersion - 567 psi - concrete break.

To speed up the thin film cure rate a higher Dion level must be used for component B (A the same as previous formula).

Component B	Pounds
Dion 3-800 LC	70.00
AEP	12.40
DMP 30	4.00
NOP	9.22
Carbon Black	0.05
RG144 Asbestos	1.50

Pot Life - 5 minutes

Bond to concrete in 25 minutes at 77°F - 287 psi.

Bond to ceramics 24 hour cure at 77°F - 723 psi - marker break (low strength buttons).

Bond to sanded reflex reflector markers 24 hour cure at 77°F - 920 psi - marker break.

Tensile bond to concrete 24 hours at 77°F - 630 psi - concrete break.
24 hours + 1 week water immersion - 159 psi - adhesive break.

7 day water absorption - 4.11%.

High water absorption is reflected in the failure in adhesion of the water immersion bond.

(5) Dion Polymercaptan - DMP 30 System

Since the AEP system offered no advantage in speed and water absorption, efforts were then concentrated on Dion poly-mercaptan-DMP 30 at stoichiometric ratios. Various liquid diluents and flexibilizers were used to find a system with lowest water absorption and having the required cure time.

Since the 70 phr level of Dion polymercaptan gave high water absorption and lower concrete shear, and the 50 phr level yielded lower water absorption, increased embrittlement and slower cure times, the 60 phr level was considered to be the best compromise.

Using the stoichiometric ratio of 60 parts of Dion and 6 parts DMP 30, nonyl phenol was added as diluent. At 15 parts nonyl phenol, acceptable physical requirements were obtained but pot life was too fast at 2 minutes. When 30 parts nonyl phenol was used, a degradation in bonding to markers was observed and the 200 psi bond to concrete was slowed down to 35 minutes. With Mobilsol 66 at 15 phr level, satisfactory physical properties were obtained but pot life was 3-1/2 minutes. This was closer to the required five minutes than that obtained with nonyl phenol. Levels of Mobilsol 66 at 18 phr just passed the required 200 psi bond in 25 minutes, at 20 phr the thin film speed slowed down to 35 minutes for 200 psi. The Mobilsol 66 limit was set at 15 phr to maintain speed of cure.

Pot Life

To increase the pot life to 5 minutes in the 60-6 Dion polymercaptan-DMP 30 system with 15 parts Mobilsol 66, 0.2 parts of 2-ethyl hexanoic acid was used.

Solid Fillers and Thixotropes

Because of the high viscosity of Shell Epon 828 or equi-valent epoxy resin, the use of solid fillers in the A component must be kept to a minimum. Asbestos RG144 at 3 phr was used to provide necessary thixotropy, leaving only 1.62 parts TiO_2 to provide whiteness. This combination of fillers gives a Brookfield viscosity of 100,000 centi-poises. In the B component using 60 parts of Dion polymercaptan, 6 parts DMP 30 and 15 parts of Mobilsol 66, considerable filler must be added to have the volume equal that of the A component which is necessary if a 1:1 volume ratio of components A and B are required. If talc is used with RG144 asbestos at 2 parts, then final viscosity is 250,000 centi-poises. This is considered too high, and for machine pumping and metering, the viscosities of the two components should be as nearly equal as possible. With #3000 Ballotini glass spheres this viscosity can be lowered to 130,000 centi-poises which is considered satisfactory. More experience is needed to determine the most favorable viscosities and thixotropic levels needed for machine use. Until then we consider the present level as adequate.

Thixotrol ST was used as a thixotropic agent and found to be very satisfactory and, except for price and higher shear and temperature requirements during mixing, could very well be used in lieu of asbestos.

Water Resistance

Water absorption curves are shown in Figure 2 for a number of various systems for comparison. The selected rapid set system designed as Laboratory Formula Am 104, although not the lowest in water absorption, shows the most satisfactory bond requirements both to markers and concrete. There seems to be a correlation between water absorption and failure in concrete tensile and shear strengths after water soak as noted in Figure 2. Am 64, 50 and 70 all failed the water soak shear requirements. Am 104 is not much lower in water absorption yet passes tensile and shear requirements. Am 104 contains stoichiometric ratios of Dion polymercaptan and DMP 30 and Am 64, 50 and 70 all have excess DMP 30. Hence, a higher level of water absorption may not necessarily lead to failures in wet tensile and shear strengths but if excess amines are present then both high water absorption and hydrolysis or chemical action with the water may take place, leading to bond failure. Of interest is the reduced water absorption in Am 84 after post curing at 140°F for 24 hours before test. Pavement temperatures often approach this value in California's Central Valleys and could be a useful asset. Apparently 24 hour cure at 77°F does not completely cure the Dion polymercaptan system. It is to be noted also that Am 104 adhesive does not soften at 140°F and does not become brittle after 140°F cure, two desirable properties as far as field performance is concerned.

Viscosity and Bonding at Elevated Temperatures

Measurements were taken at elevated temperatures of both A and B components of Am 104 using Brookfield viscometer RVT and Model C Helipath Stand and TE spindle.

Temperature °F	Centi-poises			
Component A	5 rpm	2.5 rpm	0.5 rpm	Shear Ratio
90	75,000	115,000	300,000	2.6
95	65,000	105,000	300,000	2.9
103	60,000	100,000	300,000	3.0
110	60,000	100,000	275,000	2.8
Component B				
90	75,000	120,000	350,000	2.9
95	60,000	110,000	300,000	2.7
103	60,000	100,000	250,000	2.5
110	60,000	90,000	250,000	2.8

Viscosity lowering with increased temperatures is not too extreme and even at 110°F, viscosity is only 20,000 cps below lower limit of specifications at 77°F. Both components are considered to be very well matched in viscosity. Shear ratio is very constant in both components and this should aid pumping and metering with machines.

Tensile Bond to Concrete at 105°F.

(Pot Life at 105°F was 3-1/4 minutes)

9 minutes - 143 psi - cohesive break
12 minutes - 143 psi - cohesive break
15 minutes - 175 psi - cohesive break
20 minutes - 207 psi - cohesive break

This shows the catalytic effect of the DMP 30 - Dion polymercaptan system which does not rely on heat of exotherm for cure. The level of bond strength at 105°F builds up about 5 minutes faster than that at 77°F.

Peak exotherm of a 70 gram mass was measured at 195°F.

Summary

Am 104, published as 68-F-44, meets all the adhesive requirements and has been selected as the compositional specification for a rapid set adhesive for pavement markers. Complete formula and specifications are shown in the Appendix.

This formula, based on high viscosity materials, represents the best balance with regard to viscosity, bonding and water resistance that can be obtained with the Dion polymercaptan resin.

Ideally, low viscosity resins and hardeners would be more suitable since higher filler loadings can be obtained, resulting in reduced costs per gallon and more flexibility in compounding.

Raw material costs for this adhesive at the present time are approximately $7.66 per gallon.

C. RECENT FINDINGS AND FUTURE PLANS FOR FORMULATION

One of the less desirable features of the rapid set system is the change of viscosity and flow structure or thixotropy with temperature change. For ideal field use the components should have a good thixotropic structure or "buttery" consistency which is relatively constant from 50°F to 100°F. This is accomplished readily in a system of low viscosity, but when both resin and hardener have high initial viscosities the problem becomes difficult. The use of reactive diluents in the A or epoxy resin component has been satisfactory in the past, but it slows the rate of set in thin films in the polymercaptan rapid set system to such a degree as to be of no use.

It was previously shown that attempts to lower the viscosity of the Shell Epon 828 in resin component A with most reactive diluents resulted in greater time intervals for thin films to reach an adhesive bond of 200 psi.

A low viscosity mercaptan pentaerythritol tetrathioglycolate was tried as a replacement for Dion polymercaptan in the B component. Excellent viscosity and thixotropy were obtained and speed of thin film cure was satisfactory, but water resistance very poor. The 24 hour bond strength to concrete dropped from 357 psi to 96 psi after one week of water soaking. Shear strength using a modification of the Arizona cylinder test dropped from 986 psi to zero psi after one week water soak (values were computed on the area normal to the axial load). This material appears to be very unstable, emitting a strong odor of H_2S after a few days storage. The ester linkage in this and similarly constituted polymercaptans is apparently saponified by the alkali reaction of wet concrete.

Since the use of reactive diluents proved unsuccessful in improving the flow structure of the rapid set system, work was concentrated on the use of thixotropes and fillers only.

In the A component, colloidal silica with added glycerine gives a very smooth thixotropic structure but unfortunately is unstable in storage. Blends of silica and asbestos also show storage instability due primarily to the colloidal silica. Asbestos appears to be the most suitable as a thixotrope for the A component.

In the B component, due to the lower viscosity of the Dion polymercaptan in present production, the Ballotini spheres can be replaced with talc without raising the viscosity of the component to extremes. The substitution of talc represents a cost saving since talc is approximately $0.04/lb. compared to the cost of spheres at $0.13/lb.

As a thixotrope in the B component, colloidal silica, Cab-O-Sil M5 does not give the required thixotropy even with added glycerol during shearing on the Cowles dissolver. The colloidal silica seems to give less air entrainment than asbestos, but asbestos gives the better flow structure. A compromise of the best features of each led to the trial use of equal parts of Cab-O-Sil and asbestos A144 with Sierra N. S. talc. This combination may be used in future formulations.

Off-Ratio Mixtures of Rapid Set Adhesive

The rapid set adhesive is formulated to be used in the ratio of one part A to one part B by volume. Some road applications of both rapid and standard set adhesive by mixing machines have shown variations in mixing proportions. This has been determined by chemical analysis of the hardened epoxy. Off-ratio mixing affects the rate of set and the ultimate cured strength of the epoxy. Various proportions of A and B components of standard and rapid set epoxy adhesives were mixed and rate of set (as indicated by strength at a given time) measured after 3-1/2 hours at 77°F. This was repeated with rapid set epoxy adhesive with the bond strength measured after 25 minutes at 77°F. As a measure of the "final" cured strength, two steel caps were bonded together using both adhesives, each at various ratios, and cured 24 hours at 77°F and 7 days at 140°F. Results are shown in Figures 3 and 4.

The rate of set for the standard set epoxy adhesive is most rapid with a mixing ratio of 50%-50%; the 200 psi limit being around 40%A-60%B and 60%A-40%B. The highest strengths (7 days at 140°F) occurred at ratios from 50%-50% to 60%A-40%B, dropping off a little more rapidly when mix is low on the A component. Standard set adhesive proportioned B rich is also thermoplastic and loses strength very rapidly at high temperatures. This has resulted in many failures in warm weather.

The rate of cure for the rapid set adhesive is fastest at 40%A-60%B with the 200 psi limit at 55%A-45%B and 30%A-70%B on the low A side of the curve. This means that the rate of cure may be slowed excessively if the B component is less than 47-1/2% permitted by specifications. The highest strengths (7 day cure) are achieved with 65%A-35%B but at these ratios the rate of cure is decreased excessively. These rapid set curves indicate we might be able to shift the peak of the rate of cure curve closer to the 50-50 ratio by reformulation. This would have to be done without sacrificing other properties of the present mix such as good bond to ceramic and reflective markers, low water absorption adequate cohesive and adhesive strength under moist conditions.

Some recent commercially produced lots of rapid set epoxy adhesive have failed to meet the 25 minute bond requirement of 200 psi. This has been found due to two conditions. First, most of the vendors are allowing too much air to be incorporated in the B component, making the mixed epoxy proportionally low in hardener and hence slower to set and gain strength. A second cause has been the variable density of the Mobilsol 66 diluent. When a vendor makes a batch of B component he will formulate in pounds, as per specification, but if the density of Mobilsol 66 is low, a greater yield in gallons will be produced, thus increasing the dilution of the hardener enough to slow the rate of reaction. The amount of air in the components is controlled by a specification limit. However, it is difficult, though not impossible, to manufacture the adhesive to the specification requirement for entrapped air. The only way material can be produced in the laboratory to weight per gallon specification is by heating to 170°F and evacuating to remove air. This may be achieved commercially by mixing in a closed kettle under vacuum, at 125°F.

One solution to the problem with the Mobilsol 66 would be using another diluent which has more constant properties as supplied. In this respect nonyl phenol looks promising and is now being investigated. Other than occasionally requiring 35 minutes to cure in thin films rather than the specified 25 minutes at 77°F, the rapid set formula commercially produced is performing satisfactorily when properly mixed and applied. However, more curing agent (component B) than specified must not be used since the water resistance will be adversely affected although the rate of cure would be accelerated.

Work described on Page 17, under (4) was used as a basis for the development of other useful adhesives. Epoxy binders for the repair of concrete highways and structures utilizing the polymercaptans have been developed by the California Division of Highways and are designated as Formulas Ac 51 and Ac 82. These epoxy binders cure at approximately four times the rate of the conventional polyamine and polyamide cure types.

APPENDIX

TABLE 1

Formula Number						
	1	2	3	4	5	6
Dion	60.0	60.0	60.0	60.0	70.0	70.0
DMP 30	10.0	10.0	10.0	10.0	7.0	7.0
2-E-Hex.	1.7	1.4	1.4	0.5	0.7	0.3
LP3	10.0	15.0	15.0	16.0	15.0	
Mobilsol 66						13.0
828	100	100	100	100	100	100

BOND TO MARKERS - PSI						
Ceramic						
2 hr. cure			1435	1885	1050	807
24 hr. cure	800	480	486	468	2070	1581
Reflex Reflector Sanded						
2 hr. cure			765		860	
24 hr. cure		222	356	337	1095	
Reflex Reflectors As Received						
2 hr. cure						
24 hr. cure	222	96	191	153		
Polyester						
2 hr. cure						
24 hr. cure			382	365		

TABLE II

WATER ABSORPTION

VARIOUS LEVELS DION POLYMERCAPTAN

Shell 828	Dion	DMP30	Pot Life Min.	Water Abs.%	Shore D Hardness Thin Film						
					10'	15'	20'	25'	30'	35'	40'
100	70	5.3	2	3.66	20				40	40	
100	60	6.0	1-3/4	-	20			45	50		
100	50	6.7	1-1/2	2.75	20	28	35	40	45		
100	40	7.3	2	2.04		18	25	27	35		40
100	30	8.0	2-1/4	-			18	25	30		38
100	20	8.6	3-1/2	2.09				20	22	30	
100	10	9.3	7	3.88				5	15	15	

TABLE III

WATER ABSORPTION AND CURE RATES

Dion	AEP	DMP30	NOP	25° Shore D	7 Day Water Absorption,%
30	18.6		20	10	2.26
30	16.2	1	20	25	1.94
30	13.9	2	20	30	1.98
30	10.9	3	20	30	3.24
30	10.9	3	30	25	2.21
40	17.0		20	15	1.99
40	17.0	1*	20	15	1.99
40	17.0	2*	20	15	2.36
40	17.0	2*	10	10	2.45
40	12.4	2		20	2.92
40	12.4	2	10	20	2.42
40	12.4	2	20	20	1.67
40	12.4	2	30	15	1.57
40	9.3	3	30	15	2.20
40	14.7	1	30	15	1.87
50	13.2	1	30	20	2.23
50	13.2	1	20	22	2.09
50	10.85	2	20	25	2.30
50	15.5	2*		25	4.44
60		6	20	20	2.40
60		10*	20	45	4.10
60	14	2*		25	4.69

*Excess over stoichiometric requirement.

All mixes combined with 100 parts by weight of Shell 828 epoxy resin and cured 24 hours at 77°F before water absorption test.

AEP = N-Aminoethylpiperazine

DMP 30 = 2,4,6 tri(dimethylaminomethyl) phenol

Figure 1

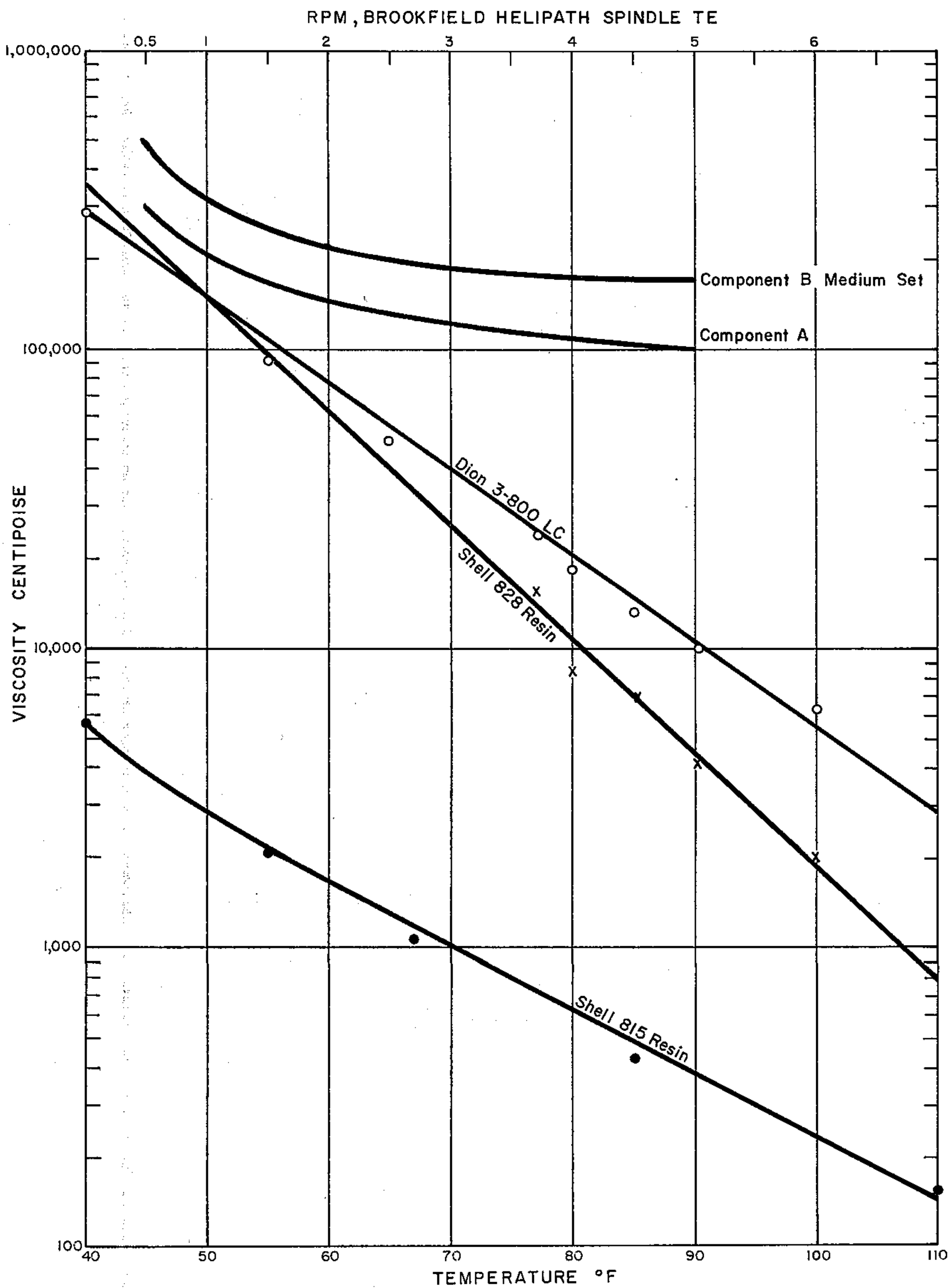
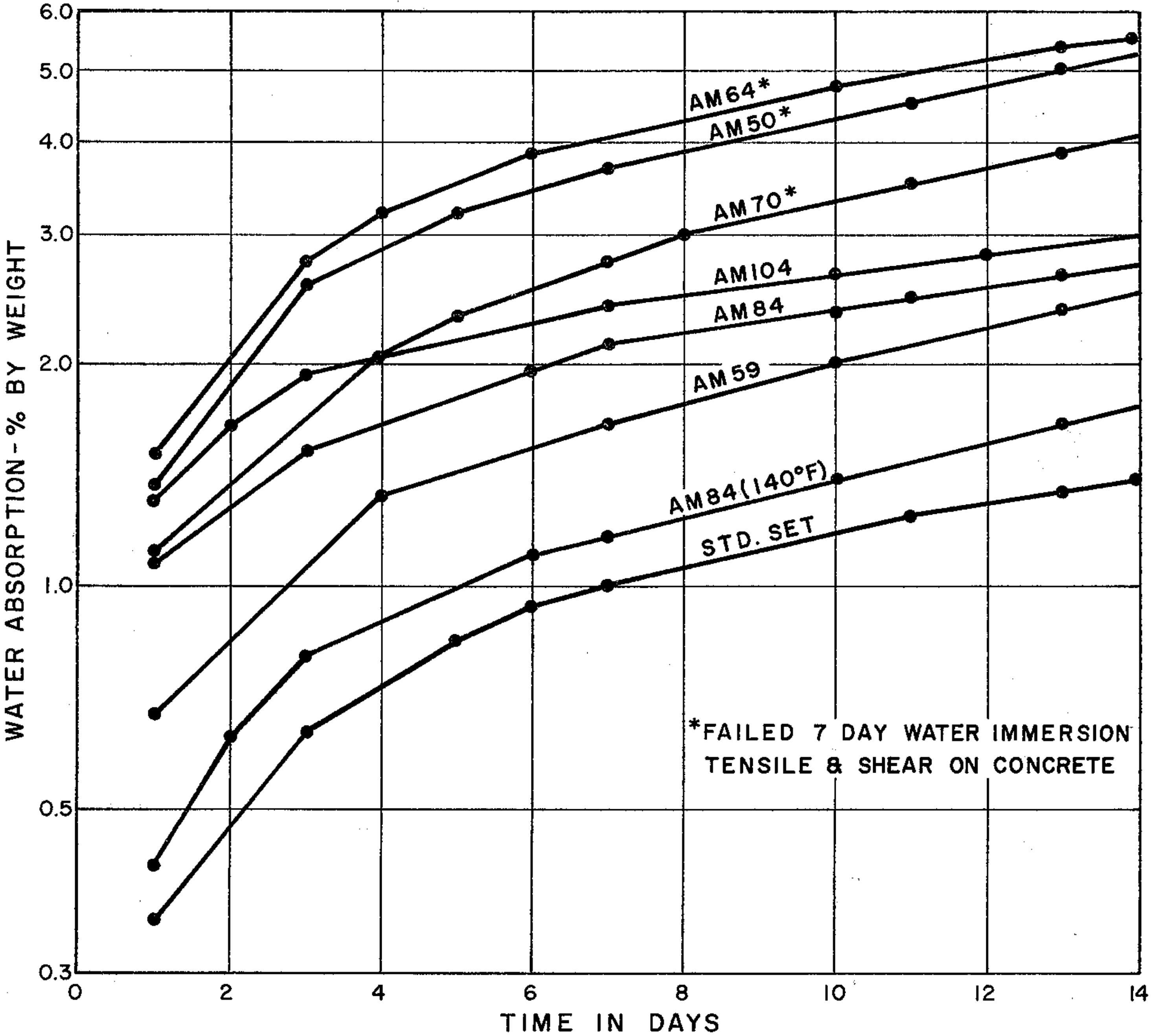

RPM, BROOKFIELD HELIPATH SPINDLE TE
0.5
1
2
3
4
5
6
1,000,000
100,000
10,000
1,000
100
VISCOSITY CENTIPOISE
Component B Medium Set
Component A
Dion 3-800 LC
Shell 828 Resin
Shell 815 Resin
40
50
60
70
80
90
100
110
TEMPERATURE °F

Figure 2

WATER ABSORPTION



COMPOSITIONS B COMPONENTS

(FILLERS NOT SHOWN)

FORMULA	DION	DMP30	AEP	NOP	LP 3	MOB 66
STD. SET			23.2	52		
AM 50	70	7			15.7	
AM 59	40	1	17	20		
AM 64	70	4	12.4	9.2		
AM 70	70	4	12.4	30		
AM 84	60	6				15
AM 104	60	6				15

Figure 3

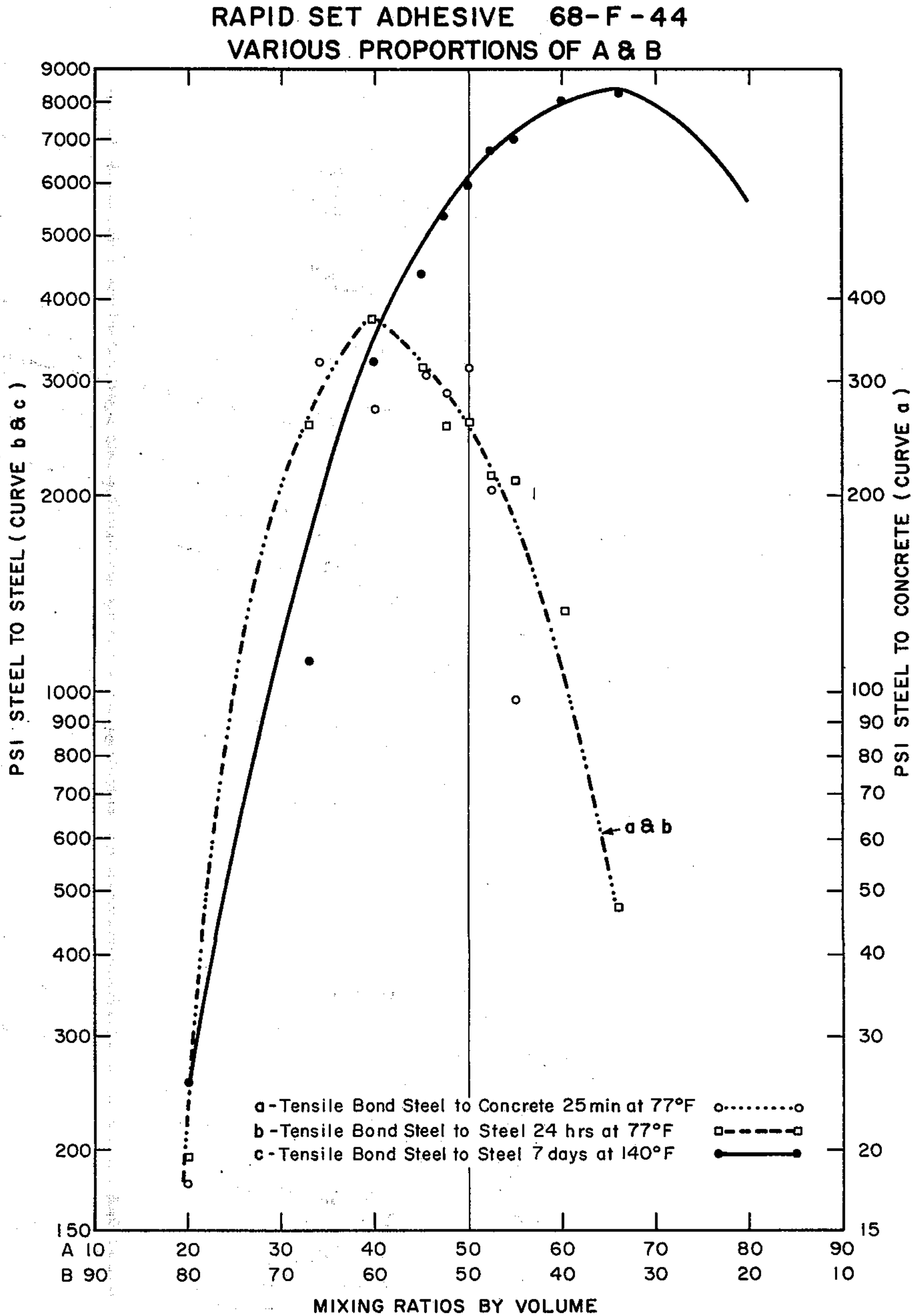
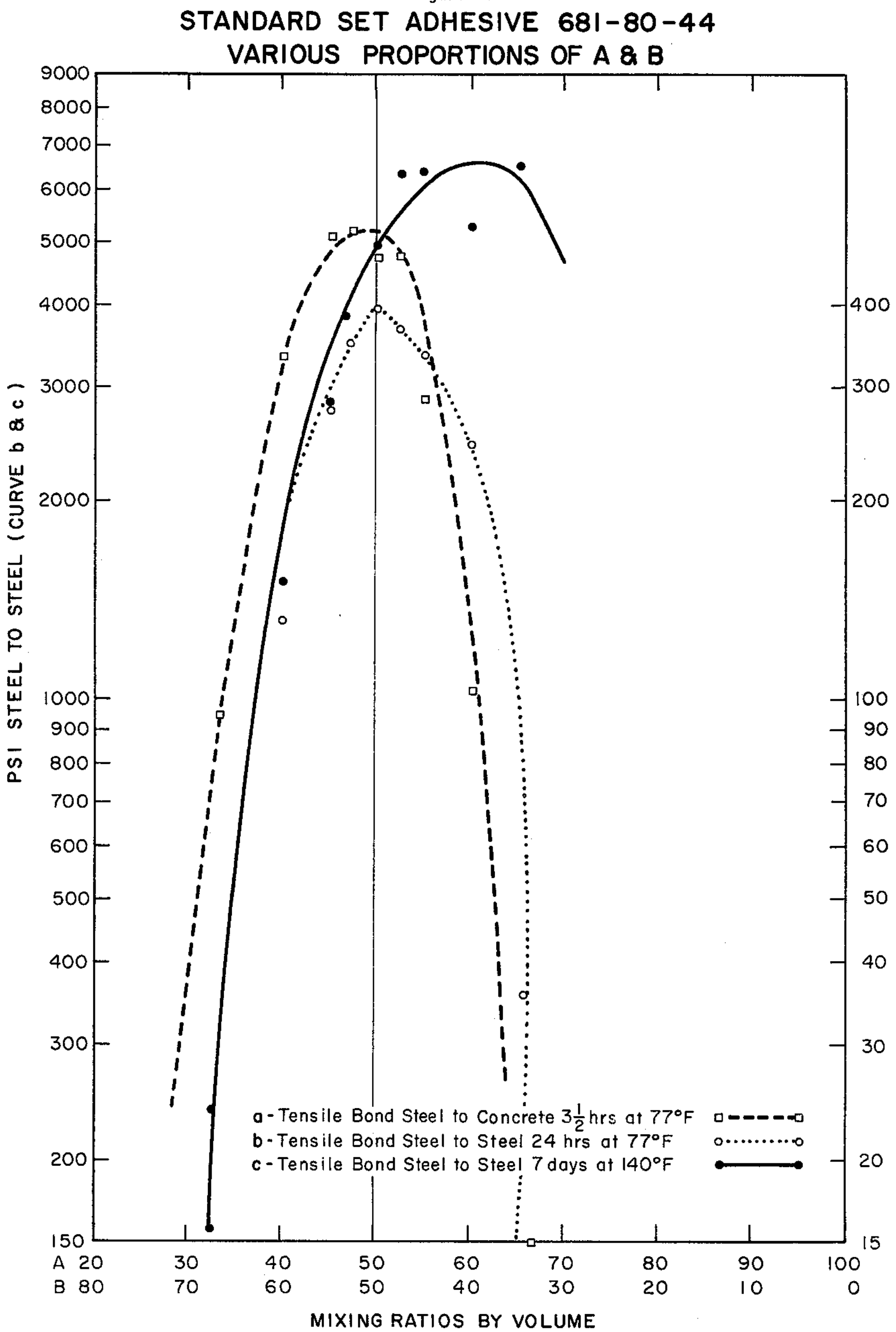

RAPID SET ADHESIVE 68-F-44
VARIOUS PROPORTIONS OF A & B
PSI STEEL TO STEEL (CURVE b & c)
PSI STEEL TO CONCRETE (CURVE a)
9000
8000
7000
6000
5000
4000
3000
2000
1000
900
800
700
600
500
400
300
200
150
400
300
200
100
90
80
70
60
50
40
30
20
15
a & b
a - Tensile Bond Steel to Concrete 25 min at 77°F
b - Tensile Bond Steel to Steel 24 hrs at 77°F
c - Tensile Bond Steel to Steel 7 days at 140°F
A 10 20 30 40 50 60 70 80 90
B 90 80 70 60 50 40 30 20 10
MIXING RATIOS BY VOLUME

Figure 4


STANDARD SET ADHESIVE 681-80-44
VARIOUS PROPORTIONS OF A & B
PSI STEEL TO STEEL (CURVE b & c)
PSI STEEL TO CONCRETE (CURVE a)
9000
8000
7000
6000
5000
4000
3000
2000
1000
900
800
700
600
500
400
300
200
150
400
300
200
100
90
80
70
60
50
40
30
20
15
a - Tensile Bond Steel to Concrete 3 1/2 hrs at 77°F
b - Tensile Bond Steel to Steel 24 hrs at 77°F
c - Tensile Bond Steel to Steel 7 days at 140°F
A 20 30 40 50 60 70 80 90 100
B 80 70 60 50 40 30 20 10 0
MIXING RATIOS BY VOLUME

State of California
Department of Public Works
Division of Highways
Materials and Research Department

TEST METHOD NO. CALIF. 425-A
March, 1968

Non-Reflective Traffic Markers

1. Bond strength to bottom surface of the marker using specified adhesive.

   a. Condition test equipment, markers and specified adhesive at 77 ± 1°F for 24 hours before test. A sandblasted 2-inch diameter steel rod or pipe cap shall be used to bond the marker and adhesive.

   b. Mix adhesive on a tin plate with a trowel or spatula until mixture shows no streaks of A or B components. Place adhesive on bottom of marker and metal surface and press firmly in place. Remove excess adhesive. Allow to cure for 24 hours at 77 ± 1°F.

   c. After curing measure the bond strength using the testing machine described in No. Calif. 420 or other testing machines. The rate of loading shall be 5,000 lbs/min. Calculate the p.s.i.

2. Glaze thickness - The glaze thickness at least 1/4-inch from the edge of the marker shall be measured on a fractured piece of the marker to the nearest 0.001-inch. Measurements shall be made by a calibrated scale microscope with a minimum magnification of 25 times.

3. Hardness.

   a. Shore "D" Hardness - Test in accordance with ASTM Designation D1706-61 and record the initial maximum reading as the hardness.

   b. Moh Hardness - The Moh hardness of the glazed marker surface shall be determined relative to the mineral orthoclase, which has a hardness of 6. Using moderate hand pressure, it must not be possible to scratch the marker with orthoclase.

4. Directional Reflectance - Test in accordance with Federal Test Method Standard No. 141, Method 6121.

5. Yellowness Index - Test in accordance with Federal Test Method Standard No. 141, Method 6131.

   NOTE: For tests 4 and 5 above the test on the glazed surface of Class III and Class IV markers shall be made on the top of the convex surface of the marker. The test on the body of Class III and Class IV markers shall be made on a clean flat surface of the marker from which the glaze has been removed. Tests on Class II markers shall be made on a clean area which has been ground or sanded flat.

6. Color - Chromaticity measurements shall be made in accordance with Test Method No. Calif. 660.

7. Autoclave - Test in accordance with ASTM Designation C424 except as follows: The specimens shall be subjected to only one autoclave cycle at 50 p.s.i. for one hour.

8. Strength - The marker shall be centered, base down, over the open end of a vertically positioned hollow metal cylinder. The cylinder shall be one-inch high with an internal diameter of 3 inches and a wall thickness of 1/4-inch. A load necessary to break the marker shall be applied at a speed of 0.2-inch per minute to the top of the marker through a one-inch diameter solid metal cylinder centered on the top of the marker. Failure shall consist of a breakage of the marker at a load of less than that specified.

9. Water Absorption - Test in accordance with ASTM Designation C 373 except as follows: Specimens selected for the water absorption test shall be whole markers and the glaze shall not be removed.

10. Titanium Dioxide - Test in accordance with ASTM Designation D 1394, beginning with paragraph 7, "Total Titanium by the Jones Reductor Method". Use a 1-gram to 1.2-gram sample of the marker exclusive of any sand, glass beads, or other substance that may be adhering to or incorporated into the bottom surface of the marker.

11. Polyester Resin Content - The polyester resin content of the marker shall be determined by ignition of a portion of the marker exclusive of any sand, glass beads, or other substance that may be adhering to or incorporated into the bottom surface of the marker. Use a 10 gram to 20 gram sample of the marker weighed into a tared crucible or heat resistant beaker. Ignite at a temperature not exceeding 550°C until no carbon residue remains.

    % Polyester Resin = Weight of sample - Weight of sample after ignition x 100 over Weight of Sample.

Reflective Traffic Markers

1. Bond strength to bottom surface of the marker using specified adhesive. Test Method same as No. 1 under non-reflective traffic markers.

2. Reflectance - The markers shall be tested at a 0.2 degree angle of divergence, and a 0° and 20° angle of incidence. The marker to be tested shall be located with the center of the reflecting face at a distance of five feet from a uniformly bright light source having an effective diameter of 0.2-inch. The photocell receptor width shall be 0.05-inch and shall be shielded to eliminate stray light. The distance from the center of the light source aperture to the center of the photocell shall be 0.21-inch. If a test distance of other than five feet is used, the source and receptor shall be modified in the same proportion as the test distance. Test results shall be calculated and reported in terms of specific intensity.

   a. Angle of incidence - The angle formed by a ray from the light source to the marker, and the normal to the leading edge of the marker face.

   b. Angle of divergence - The angle formed by a ray from the light source to the marker, and the returned ray from the marker to the measuring receptor.

   c. Specific intensity - The mean candle power of the reflected light at a given incidence and divergence angle for each foot candle at the reflector on a plane perpendicular to the incident light.

$$SI = \frac{R_L}{I_L} \times D^2$$

   Where SI = Specific Intensity.
   Where R_L = Reflected Light.
   Where I_L = Incident Light.
   Where D = Test Distance.

3. Strength - Refer to 8 above, except that failure shall consist of either (1) breakage or significant deformation of the marker at a load of less than 2,000 pounds; or, (2) significant delamination of the shell and the filler material regardless of the load required to break the marker.

TEST METHOD NO. CALIF. 425-A
EPOXY ADHESIVE INTENDED FOR USE IN BONDING TRAFFIC MARKERS TO ROAD SURFACES

1. Pot Life - The pot life shall be determined at 77 ± 1°F. Mix equal volumes of Components A and B in an 8 ounce, unwaxed paper cup 2 inches ± 1/4 inch at base to give a 170 ± 10 grams total mass. Mix 60 ± 5 seconds before timing for pot life. Test with a tongue depressor with minimum stirring. Record the time the material becomes unusable as the pot life. With most materials this will be approximately the time a hard lump forms in the center.

2. Bond Strength

   a. Clean a 4" x 4" area on a flat surface of a concrete block made with a 7-sack concrete and having a tensile strength in excess of 250 p.s.i.

   b. Use the testing machine described in Test Method No. Calif. 420 or other suitable testing press. Condition test equipment, concrete, and epoxy at test temperature for 24 hours before test. Use load rate of 5,000 lbs/min. A sandblasted 2" diameter steel rod may be used in place of pipe cap.

   c. Mix adhesive on a tin plate with a trowel or spatula for 60 ± 5 seconds. Immediately start timing, place adhesive on pipe cap and concrete surface and press firmly in place. Remove excess adhesive. Just before the required test time, insert the dynamometer hook into the cap or steel rod.

3. Shear Strength - Bond 3 concrete blocks 2" x 3-1/2" x 7" of 8-sack concrete together with the 7-inch sides parallel forming 2 areas of contact 3-1/2" x 3-1/2" by overlapping the blocks. The test specimen then has a base of 2 blocks and a second surface formed by the center block. Apply the adhesive to the contact surfaces and allow to cure for 24 hours at 77°F. Cap the base and top of middle block with an approved capping compound and test at a load rate of 10,000 lbs/min. A swivel type head must be used at the top of the testing press. Computations are based on a total area of 24.5 square inches (Shear Strength = total load/24.5) Also test after 7 days water soak.

4. Tensile Adhesion and Cohesion

   Bond the bottom surface of a sandblasted 2" diameter steel rod to the surfaces listed, cure for 24 hours at 77 ± 1°F.

4. Continued

Follow additional instructions below where applicable. Use a load rate of 5,000 lbs/min.

a. Class III ceramic marker bottom. Compute p.s.i.

b. Class III ceramic marker bottom. Post cure for 48 hours at 140°F. Condition to 77 ± 1°F and place in cold box for 24 hours at 15 ± 3°F. Allow to return to 77 ± 1°F. Test and compute p.s.i.

c. High strength concrete; 2" thick 3-1/2" wide by 7" long. Steel rod bonded to the 3-1/2" x 7" surface. Test and compute p.s.i. Any test failing in concrete below specification value shall be repeated.

d. High strength concrete specimen prepared as in 4c above. Soak in distilled water for 7 days. Remove from water and test immediately. Compute p.s.i. Any test failing in concrete below specification value shall be repeated.

5. Viscosity - The viscosity of each component shall be measured in 3/4 filled standard round quart paint can.

Stir the components vigorously for 30 seconds with a spatula. Remove entrained air by vigorous tamping and measure viscosity within 10 minutes after stirring. Use a Brookfield viscometer, Model RVT at 5.0 RPM with a Model C Brookfield Helipath Stand and Helipath Spindle specified. Use weight included in spindle set. Component and ambient temperature is to be 77 ± .5°F at time of measurement. Readings shall be taken at approximately the center of the vertical travel of the spindle.

6. Shear Ratio - $\text{Shear Ratio} = \dfrac{\text{Viscosity at 0.5 RPM}}{\text{Viscosity at 2.5 RPM}}$

Readings for shear ratio shall be taken at the same time as the viscosity at 5 RPM.

7. Lbs/Gallon

Determine as in Federal Test Method Standard No. 141A Method 4184.1.

8. Percentage of Air

The entrapped air on the Rapid Set Type shall be removed by applying a high vacuum to each component heated to 175 to 180°F. The sample shall also be vibrated or tamped to

8. Continued

facilitate air removal. Allow sample to cool to 77 $\pm$ 3°F before measurement of Lbs/gal as in 7 above. The percentage of air shall be calculated as follows:

$$\% \text{ air} = \frac{\text{Lbs/gal (air removed)} - \text{Lbs/gal (as received)} \times 100}{\text{Lbs/gal as received}}$$

STATE SPECIFICATION 681-80-44

STANDARD SET TYPE

Composition:

Component A	Parts by Weight
Epoxy Resin[1]	100.0
Titanium Dioxide, TT-P-442, Type III or IV	7.31
Resin Grade Asbestos[2]	5.00
Talc[3]	37.64

Component B	
N-Aminoethyl piperazine[4]	23.16
Nonylphenol[5]	52.00
Carbon Black, TT-P-343, Form I, Class B	0.22
Talc[3]	77.37
Resin Grade Asbestos[2]	1.00

[1]Viscosity, 5-7 poises at 25°C.; epoxide equivalent 175-195; Color (Gardner) 5 maximum; manufactured from epichlorohydrin and bisphenol A. The reactive diluent shall be butyl glycidyl ether.

[2]Specific gravity, grams per ml., 2.45; moisture content, % by weight, 2.0 maximum; surface area, square meters per gram, 60 approximately; reflectance, G. E. brightness, 72-76; nature of surface charge, electropositive (cationic); pH in water, 9.5; bulking value, gallons per 100 lbs., 4.8; oil absorption (DOP), pounds per 100 lbs., 120; refractive index, n_d 25°C., 1.54-1.56; wet bulk density in water, after dispersion, 2 grams per liter, settling after 1 hr., 100 ml. clear maximum; dry bulk density, pounds per cubic foot, 4.

[3]Percent passing U.S. No. 325 sieve, 94-96; maximum particle size, 70 microns; oil absorption (Gardner-Coleman), 6-7 ml. per 20 grams; fineness in oil (Hegman) 1-2; specific surface, 0.5-0.6 square meter per gram; consistency (40% suspension in linseed oil) 55-60 KU.

[4]Color (APHA) 50 maximum; amine value 1250-1350 based on titration which reacts with the 3 nitrogens in the molecule; appearance clear and substantially free of suspended matter.

[5]Color (APHA) 50 maximum; hydroxyl number 245-255; distillation range, °C at 760 mm first drop 295 minimum, 5% 298 minimum, 95% 325 maximum; water, % (K.F.) 0.05 maximum.

Directions for Use:

Any settling of fillers or pigments in Component A or B shall be completely redispersed to provide a homogeneous mix before the components are used. Just before use, components A and B shall be mixed in a one-to-one ratio by volume.

When the Rapid Set Type adhesive is used, the components shall be mixed by a 2-component type automatic mixing and extrusion apparatus. The temperature of the Rapid Set Type adhesive shall be maintained at 65°F. to 85°F. before mixing. The temperature of the Standard Set Type adhesive shall be maintained at 60°F. to 100°F. before mixing. Any heating of epoxy adhesive shall be done by the application of indirect heat.

STATE OF CALIFORNIA—TRANSPORTATION AGENCY

RONALD REAGAN, Governor

DEPARTMENT OF PUBLIC WORKS
DIVISION OF HIGHWAYS
MATERIALS AND RESEARCH DEPARTMENT
5900 FOLSOM BLVD., SACRAMENTO 95819

REVISION OF THIS SPECIFICATION
EXPECTED WITHIN 1 YEAR (SEE TEXT)

May, 1968

EPOXY ADHESIVE FOR PAVEMENT MARKERS
RAPID SET TYPE

STATE SPECIFICATION 68-F-44

Composition of Adhesive

PACKAGE A

	Parts by Weight
Epoxy Resin[1]	100.00
Resin Grade Asbestos[2]	3.00
Titanium Dioxide, TT-P-00442, Type IV	1.62

PACKAGE B

High functionality polymercaptan hardener[3]	60.00
2,4,6-Tri(dimethylaminomethyl) phenol[4]	6.00
Alkyl substituted polynuclear aromatic oil[5]	15.00
2-Ethyl Hexanoic Acid[6]	0.20
Carbon Black TT-P-343, Form 1, Class B	0.05
Resin Grade Asbestos[2]	2.00
No. 3000 Ballotini glass spheres[7]	36.36

[1] Di glycidyl ether of bisphenol A, viscosity, 100-160 poise at 25°C; epoxide equivalent 180-200. Color, Gardner 1933, 3 max. No reactive diluent shall be used.

[2] Specific gravity, 2.45; moisture content, percent by weight, 2.0 maximum; surface area, square meters per gram, 60 approximately; reflectance, G.E. brightness, 72-76; nature of surface charge, electropositive (cationic); pH in water, 9.5; bulking value, gallons per 100 lbs., 4.8; oil absorption (DOP), pounds per 100 lbs., 120; refractive index, n_d 25°C., 1.54-1.56; wet bulk density in water, after dispersion, 2 grams per liter, settling after 1 hr., 100 ml. clear maximum; dry bulk density, pounds per cubic foot, 4.

[3] Liquid polymercaptan resin, viscosity 150 poise at 25°C; specific gravity 1.15; mercaptan value, 3.6 meq/gram. Color, Gardner - 1933, 1. Must match infra-red absorption curve shown in this specification.

4 Formula weight 265; specific gravity at 25°/25°C, 0.973; refractive index 1.514 at 25°C; distillation range 96% at 130 to 160°C (0.5 - 1.5 mm.); flash point, Tag open cup, 300°F minimum; water content 0.06% maximum.

5 High boiling, alkyl substituted polynuclear aromatic oil. Weight per gallon at 77°F, 9.00 - 9.15; flash point, °F, Pensky Martens Closed Cup (ASTM E134), 350 - 390; viscosity SU at 100°F, 90 - 120; mixed aniline point (ASTM D-1012), °F, 72 maximum; color, Gardner, 1933, 12 maximum; viscosity, Gardner-Holdt at 77°F, A-C. Percent Aromatic 95 minimum

Distillation Range

Percent Distilled	°F
1BP	580 Min.
5	610-640
10	620-660
50	650-700
90	680-740

6 Practical grade, B.P., 112-114°C, 8 mm., molecular weight, 144.21.

7 Spherical shaped, clear, soda-lime glass, Moh hardness, 6; specific gravity 2.48; refractive index 1.525; oil absorption, ASTM D-281-31, 17; free moisture 0.1% maximum; surface pH, 9.5; bulking density, 11.5 - 12 lbs. per gallon; SiO_2, 68% minimum; not to contain more than 0.10% free magnetic iron particles; particle size, U.S. Standard Screen No. 325 and finer (44 microns and finer) percent passing, 100; spheres shall be uncoated. The distribution of particle size shall be such that the properties of Package B and the mixed adhesive shall meet those required in this specification.

NOTE: If the manufacturer of this adhesive is in doubt as to what materials meet the above requirements, he should contact the Materials and Research Department of the Division of Highways.

Infrared absorption curves for the extracted vehicles of Package A and B must match those shown in this specification.

When Package A and Package B are mixed in the proportion of 1 volume of package A to 1 volume of package B, the mixed adhesive shall have the following properties.

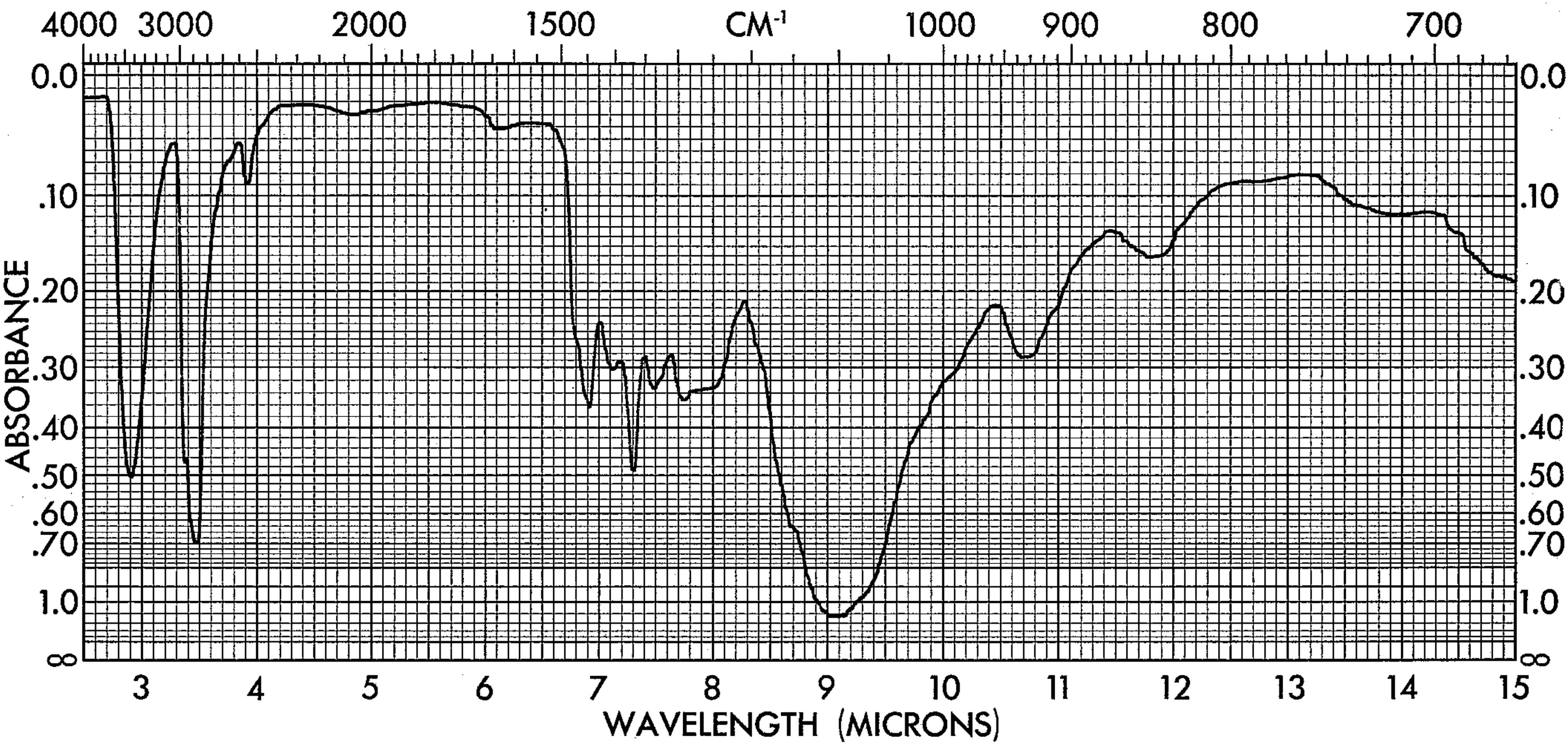
All tests shall be performed in accordance with Test Method No. Calif. 425.

Test		Requirements
(1)	Pot Life	5 minutes Min.
(2)	Bond Strength to Concrete, Time (Maximum) to reach at least 200 psi	
	at 77°F ± 1°F	25 minutes
	at 50°F ∓ 1°F	45 minutes
	at 30°F ∓ 1°F	85 minutes
(3)	Shear Strength on Concrete (Minimum)	
	24 hours at 77°F ± 3°F	1000 psi
	24 hours at 77°F ∓ 3°F plus 7 days water soak at 77°F ± 3°F	700 psi
(4)	Tensile Adhesion and Cohesion Bond of 2-inch diameter bottom of a steel rod to the following:	
	(a) Class III ceramic marker bottom	1200 psi Min.
	(b) Class III ceramic marker bottom including post cure	1200 psi Min.
	(c) Reflective pavement marker bottom	400 psi Min.
	(d) Class II marker bottom	500 psi Min.
	(e) High strength concrete	550 psi Min.
	(f) Same as in (e) plus 7-day water soak	400 psi Min.
(5)	Viscosity Centipoise	T.E. Spindle
	Component A at 77°F	0.80×10^5 to 1.3×10^5
	Component A at 55°F	1.3×10^5 to 5.0×105
	Component B	As Above
(6)	Shear Ratio Minimum	77°F - 55°F
	Component A	1.8 - 1.5
	Component B	1.8 - 1.5
(7)	Lbs./Gallon	
	Component A	9.7 - 10.0 *
	Component B	11.0 - 11.4 *
(8)	Color	Approximately that of color No. 16165 of Federal Standard No. 595
(9)	Skinning, Components A and B	None

*No more than 2.5% air permitted.

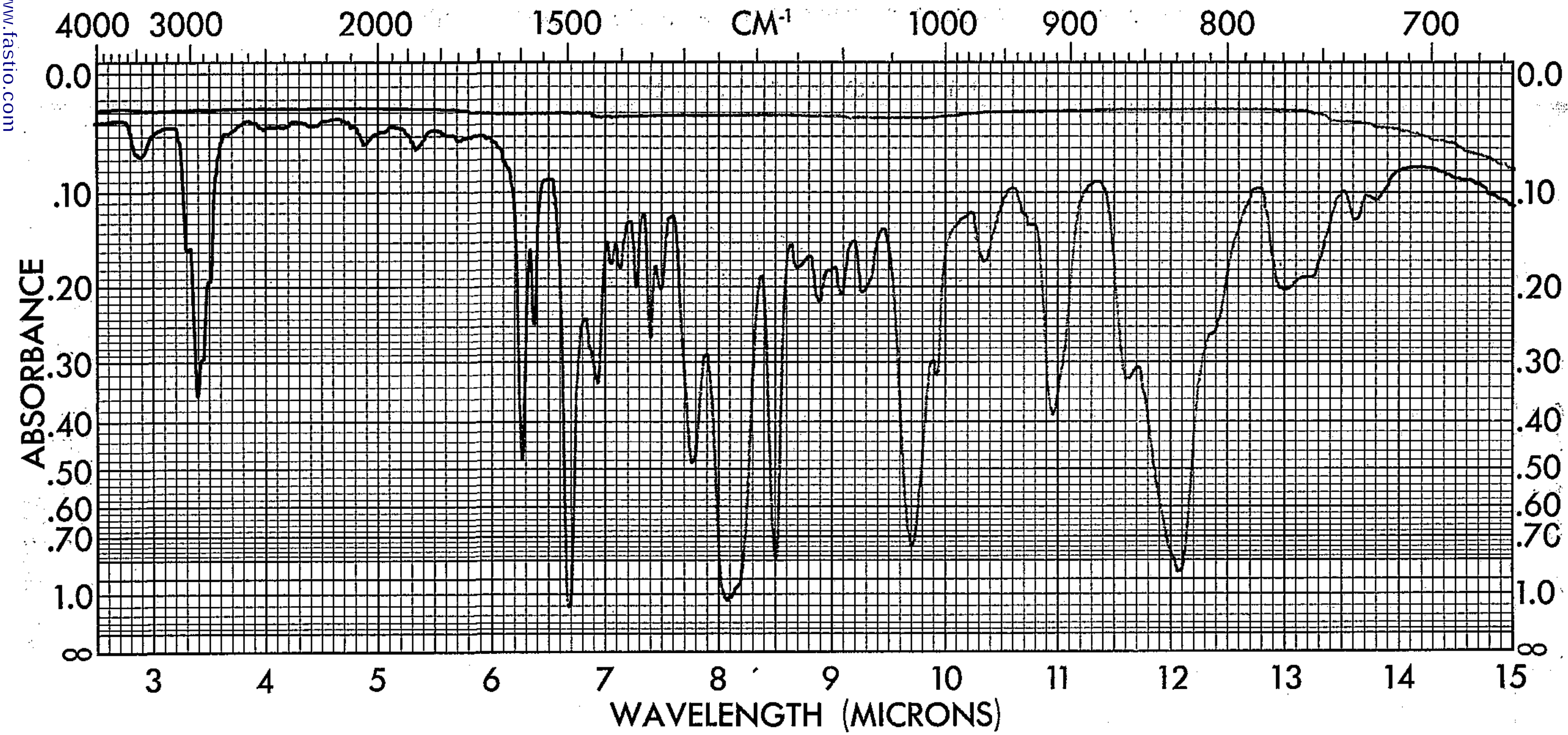
(10) Storage Stability

The Components A and B shall not change in viscosity and shear index by more than ± 15 percent when stored for 2 weeks in closed containers at 115°F ± 3°F. The adhesive shall meet all other requirements for 12 months from the date of manufacture. There shall be no hard settling of the fillers. Any settling shall be easily redispersed with a paddle.



INFRARED ABSORPTION CURVE

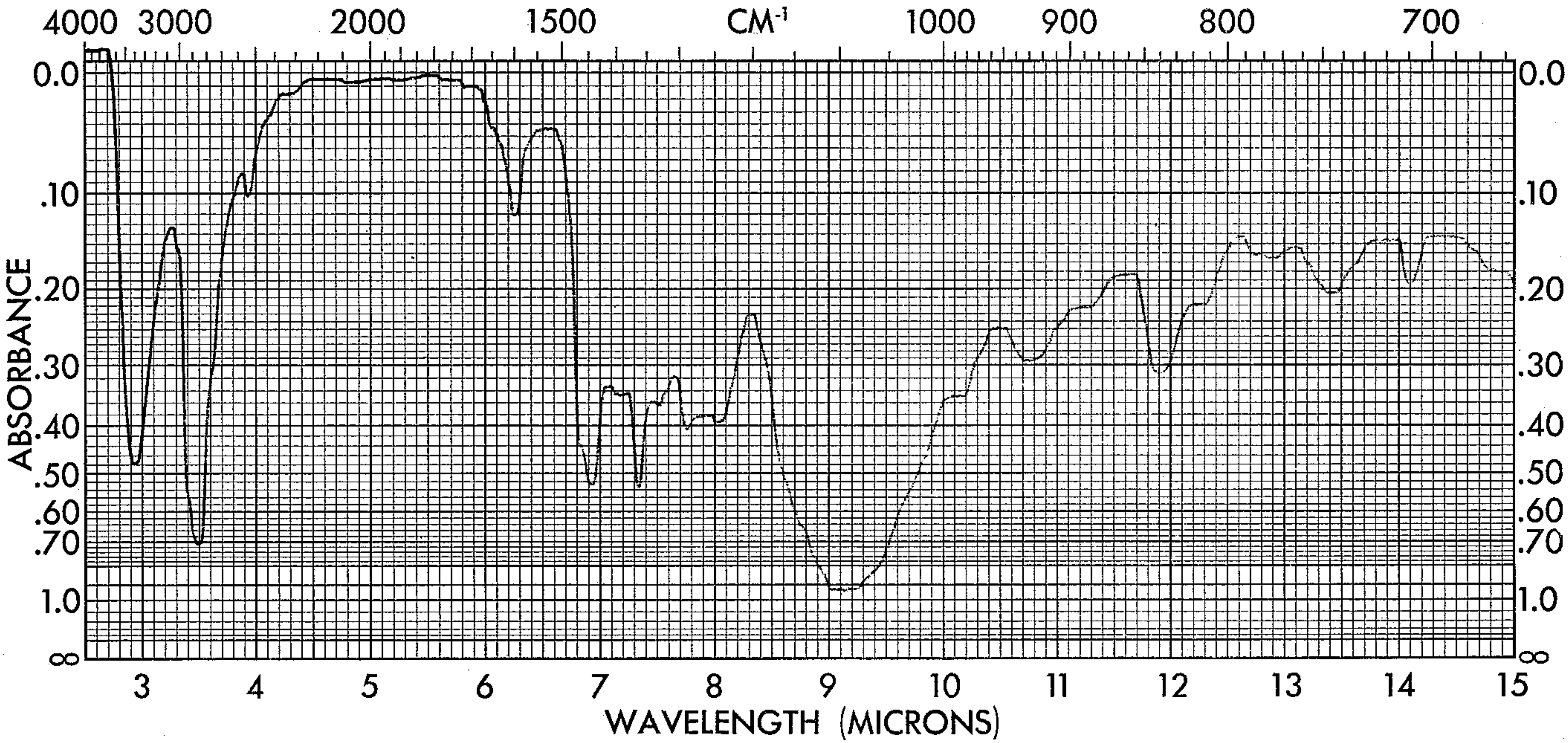
LIQUID POLYMERCAPTAN RESIN, STATE SPECIFICATION 68-F-44



INFRARED ABSORPTION CURVE

EXTRACTED VEHICLE COMPONENT A

RAPID SET ADHESIVE, STATE SPECIFICATION 68-F-44



INFRARED ABSORPTION CURVE

EXTRACTED VEHICLE COMPONENT B

RAPID SET ADHESIVE, STATE SPECIFICATION 68-F-44

Packaging and Labeling of Adhesive

Each adhesive component shall be packaged in containers not larger than 5 gallons in volume. The containers shall be new steel, not less than 24-gage and shall otherwise meet Interstate Commerce shipping standards. Each container shall be clearly labeled with the State Specification 68-F-44, designation (Component A or B), Rapid Set Type, manufacturer's name, date of manufacture, batch number (a batch shall consist of a single charge of all components in a mixing chamber), directions for mixing, and the following warning:

CAUTION

This material will cause severe dermatitis if it is allowed to come in contact with the skin or eyes. Use gloves and protective creams on the hands. Should this material contact the skin, wash thoroughly with soap and water. Do not attempt to remove this material from the skin with solvents. If any gets in the eyes, flush for 10 minutes with water and secure immediate medical attention.

Directions for Mixing

Any settling of fillers or pigments in Package A or B shall be completely redispersed to provide a homogenous mix before the packages are used.

When the Rapid Set Type adhesive is used, the components shall be mixed by a 2-component type automatic mixing and extrusion apparatus, and the markers shall be placed within 60 seconds after the adhesive has been mixed and extruded. The temperature of the Rapid Set Type adhesive shall be maintained at 60°F to 85°F before mixing. Any heating of epoxy adhesive shall be done by the application of indirect heat.

The mixing equipment for the epoxy adhesive shall properly meter the 2 components in a 1:1 ratio, $\pm$ 5% by volume of either component. At the beginning of each day and at any other time ordered by the Engineer, the ratio shall be checked by the Contractor in the presence of the Engineer. This check shall be made by disconnecting the mixing heads, or using suitable bypass valves, and filling 2 suitable containers with the unmixed components. The mixing head shall properly mix the 2 components so that there is no trace of black or white streaks in the mixed material.

The Rapid Set Type adhesive shall not be used when either the pavement or the air temperature is less than 30°F. No markers shall be installed if the relative humidity of the air is greater than 80 percent or if the pavement is not surface dry.